



RÓzanski, K., Chmura, L., Gałkowski, M., NCKI, J., Zimnoch, M., Bartyzel, J., & O'doherty, S. (2017). Monitoring of Greenhouse Gases in the Atmosphere – A Polish Perspective. *Papers on Global Change IGBP*, 23(1), 111-126. <https://doi.org/10.1515/igbp-2016-0009>

Publisher's PDF, also known as Version of record

License (if available):  
CC BY-NC-ND

Link to published version (if available):  
[10.1515/igbp-2016-0009](https://doi.org/10.1515/igbp-2016-0009)

[Link to publication record in Explore Bristol Research](#)  
PDF-document

This is the final published version of the article (version of record). It first appeared online via De Gruyter at <https://doi.org/10.1515/igbp-2016-0009> . Please refer to any applicable terms of use of the publisher.

## University of Bristol - Explore Bristol Research

### General rights

This document is made available in accordance with publisher policies. Please cite only the published version using the reference above. Full terms of use are available:  
<http://www.bristol.ac.uk/red/research-policy/pure/user-guides/ebr-terms/>

## MONITORING OF GREENHOUSE GASES IN THE ATMOSPHERE – A POLISH PERSPECTIVE

KAZIMIERZ RÓŻAŃSKI, ŁUKASZ CHMURA, MICHAŁ GAŁKOWSKI,  
JAROSŁAW NĘCKI, MIROSLAW ZIMNOCH, JAKUB BARTYZEL

Faculty of Physics and Applied Computer Science,

AGH University of Science and Technology

30-059 Kraków, Al. Mickiewicza 30, Poland

e-mail: rozanski@agh.edu.pl, lukasz.chmura@fis.agh.edu.pl,

michal.galkowski@fis.agh.edu.pl, necki@agh.edu.pl, zimnoch@agh.edu.pl,

jakub.bartyzel@fis.agh.edu.pl

SIMON O'DOHERTY

Atmospheric Chemistry Research Group, University of Bristol, Cantock's Close,

Clifton, Bristol BS8 1TS, United Kingdom

e-mail: s.odoherty@bristol.ac.uk

**ABSTRACT:** An overview of systematic observations of the trace-gas composition of the atmosphere over southern Poland is presented, against the background of data available for other greenhouse gas (GHG) monitoring stations in Europe. The results of GHG monitoring for three major greenhouse gases ( $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{N}_2\text{O}$ ) are discussed. Measurements were performed at two locations of contrasting characteristics, i.e. (i) the high-altitude mountain station of Kasprowy Wierch in the High Tatras, representing atmospheric conditions relatively free of local influences, and (ii) an urban station located in the Krakow agglomeration. The GHG data available for the Kasprowy Wierch station were compared with relevant data available for two marine reference stations (Mace Head, Ireland and Terceira Island, Azores), and two continental stations (Hohenpeissenberg, Germany and Pallas-Sammaltunturi, Finland). The growth rates for the  $\text{CO}_2$  mole fraction recorded at these five stations reveal only small temporal changes that almost coincide, leading to a quasi-linear increase of the  $\text{CO}_2$  mixing ratio over the European continent over the past 20 years. While  $\text{N}_2\text{O}$  observations also reveal a steady increase over this

time period, the mole fraction accounted for by  $\text{CH}_4$  is increasing again, after a period of stagnation in the years 2001–2007. The impact of continental sources of  $\text{CH}_4$  and  $\text{N}_2\text{O}$  is seen clearly in the Kasprowy Wierch records. The mean departure between the  $\text{CH}_4$  mixing ratios recorded at Kasprowy Wierch and at the marine reference stations in the period 1994–2014 is of 27.3 ppb, and stems from continental emissions of this gas originating mainly from anthropogenic activities (leaking natural-gas distribution networks, landfills and livestock). For  $\text{N}_2\text{O}$ , a departure of 1 ppb was observed for the period 2009–2014. Comparison of quasi-continuous measurements of  $\text{CO}_2$ ,  $\text{CH}_4$  and  $\text{N}_2\text{O}$  mixing ratios made in the urban atmosphere of Krakow and at the regional reference site Kasprowy Wierch (located approximately 100 km away), allows for a deeper insight into the mechanisms controlling daily variations in atmospheric mixing ratios of these gases at the two sites. The development of a nocturnal inversion layer in the atmosphere above the city leads to local enhancements of  $\text{CO}_2$ ,  $\text{CH}_4$  and  $\text{N}_2\text{O}$  mole fractions in the Krakow atmosphere during the night hours, with these exceeding the baseline level significantly.

**KEY WORDS:** monitoring, trace gases, atmosphere, greenhouse effect.

## INTRODUCTION

Greenhouse gases (GHGs) are trace compounds whose specific physical properties ensure them of an important role where the radiative balance of Earth's atmosphere is concerned (IPCC 2013). The most important of the gases are water vapour ( $\text{H}_2\text{O}$ ), carbon dioxide ( $\text{CO}_2$ ), methane ( $\text{CH}_4$ ) and nitrous oxide ( $\text{N}_2\text{O}$ ). By way of the natural (non-augmented) greenhouse effect these ensure comfortable temperatures at the Earth's surface. However, anthropogenic activities have been modifying atmospheric composition in different ways; among which perhaps the most important is the overall increase in the mole fractions accounted for by the aforesaid major greenhouse gases – a process ongoing since the mid-19<sup>th</sup> century (IPCC 2013). Nowadays, the composition of the atmosphere is being watched on the basis of increasing awareness, on the local, regional or global scales.

Although isolated measurements of  $\text{CO}_2$  mixing ratios in the atmosphere were already being made using chemical methods by the second half of the 19<sup>th</sup> century, it was Charles D. Keeling around a century later who realised the importance of regular measurement of GHGs in the atmosphere (Keeling 1960). It was he who started regular measurements of atmospheric  $\text{CO}_2$  mole fractions in June 1956, at the Mauna Loa Observatory on Hawaii island in the Pacific Ocean, at an elevation of 3397 m a.s.l. ([www.esrl.noaa.gov/gmd/obop/mlo/](http://www.esrl.noaa.gov/gmd/obop/mlo/)).

Today, regular observations of the trace-gas composition of the atmosphere are made, via global and regional monitoring networks, such as Global Atmosphere Watch ([www.wmo.int/pages/prog/gaw/](http://www.wmo.int/pages/prog/gaw/)), NOAA Earth Systems Research Laboratory ([www.esrl.noaa.gov/gmd/](http://www.esrl.noaa.gov/gmd/)) or the Advanced Global Atmospheric Gases Experiment

([www.agage.eas.gatech.edu](http://www.agage.eas.gatech.edu)). New regional initiatives also now being pursued include the Integrated Carbon Observation System ([www.icos-infrastructure.eu](http://www.icos-infrastructure.eu)), and the National Ecological Observatory Network ([www.neonscience.org](http://www.neonscience.org)).

If properly designed and maintained, atmospheric monitoring networks can serve several functions. First, they document spatial and temporal evolution of the composition of Earth's atmosphere as a result of natural processes and human activities. Second, they help in the assessment of the effectiveness of international agreements aimed at reducing atmospheric mixing ratios of key trace substances, such as CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>O, influencing the radiative balance of Earth's atmosphere, as well as substances depleting stratospheric ozone reserves (e.g. N<sub>2</sub>O, chlorofluorocarbons, and others). Finally, they provide valuable data for current research on the global carbon cycle (*Global Carbon Project* 2015), and the behaviour of various trace substances in the Earth-atmosphere system.

Historically, observations of the trace-gas composition of Earth's atmosphere relied either on a limited number of remote sites at which air samples were collected for subsequent laboratory analyses, or on an even more limited number of *in-situ* measurement sites such as Mauna Loa Observatory. Atmospheric observations at those remote locations were used in simple box-type models to derive estimates of atmospheric budgets of greenhouse gases or ozone-depleting substances on a global scale. The rapid growth of scientific understanding and computational power allowed for expansion of these simple modelling tools, and for the inclusion of more-sophisticated representations of atmospheric processes. This provided an even more detailed picture of the behaviour of trace gases in the present-day atmosphere, on various temporal and spatial scales. These advanced numerical tools (models) rely heavily on atmospheric observations. With increased complexity of representation of atmospheric processes in these models, there is a growing need for observational data. Regional analyses of greenhouse gas budgets are subject to strict requirements concerning temporal resolution, spatial extent, precision and accuracy of observational data. These requirements are reflected in the accuracy and precision levels set for stations monitoring greenhouse gas by final data users, i.e. researchers or policymakers (e.g. WMO 2013).

Stationary, ground-based monitoring networks are not the sole source of information about GHG mixing ratios in the atmosphere. Nowadays, selected GHGs can be studied by remote sensing via dedicated satellites, as another option by which information about the trace-gas composition of Earth's atmosphere can be obtained. Satellite observations offer extensive spatial coverage, combined with a possibility of information being provided on vertical profiles of measured atmospheric constituents. Disadvantages of remote sensing include lower measurement precision, lower temporal resolution and uneven spatial and temporal coverage (e.g. Takagi *et al.* 2011, Nassar *et al.* 2014). Currently, the usage of remote sensing in GHG monitoring of lower troposphere is limited to CO<sub>2</sub> and CH<sub>4</sub>, though the release of a new generation of satellites may also make information retrieval about other atmospheric constituents (including N<sub>2</sub>O) a real possibility in the near future.

Here we present an overview of systematic observations of the trace-gas composition of the atmosphere over the European continent, with the emphasis placed on southern Poland (Fig. 1A). The presentation here is of the monitoring results for the three major greenhouse gases ( $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{N}_2\text{O}$ ). In Poland, regular measurements of atmospheric GHG compositions are made at three locations of contrasting characteristics: (i) the high-altitude mountain site of Kasprowy Wierch in the High Tatras, which represents typical conditions higher up in the atmosphere, and relatively free of local influences, (ii) a high tower located close to the city of Białystok in the north-east corner of the country, operated by the Max Planck Institute for Biogeochemistry in Jena, Germany, and representing the lowland atmosphere, with a high impact due to the local biosphere and limited anthropogenic influences, and (iii) an urban site (Krakow), representing a typical urban atmosphere exposed to numerous sources of GHGs (not least heating, transport, and others). Here, only the data originating from the Kasprowy Wierch and Krakow sites will be presented and discussed, in relation to the results available for other GHG monitoring stations in Europe.



Figure 1. A – Locations of the GHG monitoring stations; KAS – Kasprowy Wierch, Poland; MHD – Mace Head, Ireland; HPB – Hohenpeissenberg, Germany; AZR – Terceira Island, Azores; PAL – Pallas-Sammaltunturi, Finland. Inserted pictures show the surroundings of the stations at Kasprowy Wierch (B) and in Krakow (C)

The measurements of atmospheric mixing ratios of CO<sub>2</sub> and CH<sub>4</sub> at the Kasprowy Wierch station go back to 1994 (Nęcki *et al.* 2003). N<sub>2</sub>O has been measured there regularly, since 2009 (Gałkowski 2015). Measurements of CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>O mixing ratios in the Krakow atmosphere have been being made on an intermittent basis since 2003 (Chmura *et al.* 2008, Chmura 2009, Gałkowski 2015).

## DESCRIPTION OF MONITORING SITES

The Kasprowy Wierch station (49°14' N, 19°59' E, 1989 m a.s.l., air intake at 4 m a.g.l.) is situated on top of the Kasprowy Wierch peak located in the Tatra Mountains, at the intersection of three main valleys on the border between Poland and Slovakia (Fig. 1B). Since Kasprowy Wierch is situated within the transition zone between the free troposphere and the planetary boundary layer, and is relatively free of local influences, this site is considered a regional reference station for trace gas measurements in the lower atmosphere over Central and Eastern Europe.

The GHG monitoring site in Krakow (50°04' N, 19°55' E, 220 m a.s.l.) is situated on the University campus located in the western part of the city, bordering recreation and sports grounds (Fig. 1C). The air intake is placed approx. 40 m above the local ground. Krakow is located some 100 km north of the Tatra Mountains, in which the Kasprowy Wierch station operates. With about one million inhabitants, rapidly growing car traffic and significant industrial activities, the Krakow agglomeration represents a typical urban environment in Eastern Europe. Characteristic features of the local climate are generally weak winds and frequent thermal inversions in the lower troposphere, extending over several days at times, particularly during the winter season. These factors favour accumulation of trace gases originating from surface emissions in the lower atmosphere over the city.

## METHODS

Atmospheric mole fractions of CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>O are measured at Kasprowy Wierch and in Kraków using automated gas chromatographs (Nęcki *et al.* 2003, Gałkowski 2015). This analytical set-up allows for the monitoring of CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>O in quasi-continuous mode, with consecutive measurements performed every 15–30 minutes, in a standard–sample–standard sequence. Each working standard is calibrated against two reference gases certified by the NOAA Earth Systems Research Laboratory, which provide a direct connection to the internationally recommended measurement scales for all three gases analysed. The scales used are WMO X2007 for CO<sub>2</sub>, NOAA 2004 for CH<sub>4</sub> and NOAA 2006A for N<sub>2</sub>O. In addition, both sites are participating in inter-laboratory comparison programmes to ensure adequate measurement intercomparability (CUCUMBER 2016).

## RESULTS AND DISCUSSION

This section presents the results of GHG monitoring available for the Kasprowy Wierch and Krakow stations, going on to discuss them in the context of data available for other GHG monitoring sites in Europe.

### CARBON DIOXIDE

The record for CO<sub>2</sub> mixing ratios available for the Kasprowy Wierch station is as shown in Figure 2. The record covers the time period from September 1994 through to December 2015. Three types of data are presented in this figure. First, daily means for the measured CO<sub>2</sub> mixing ratios are shown in the background (in orange), these being calculated from the results of quasi-continuous monitoring, after an appropriate, three-step data selection procedure has been applied to the raw measurement results. These selected data represent the background conditions at the station (Nęcki *et al.* 2003). Second, daily mean values were further smoothed using the routine recommended by NOAA (CCGvu 4.40 – Thoning *et al.* 1989), resulting in the curve shown in blue. Finally, the trend curve derived from daily means after deseasoning and further smoothing of the data following the CCGvu4.40 routine, is shown in black. The mole fraction for CO<sub>2</sub> at Kasprowy Wierch has increased by 11.8%, from 361.9 ppm in 1994 to 403.9 ppm in 2015.

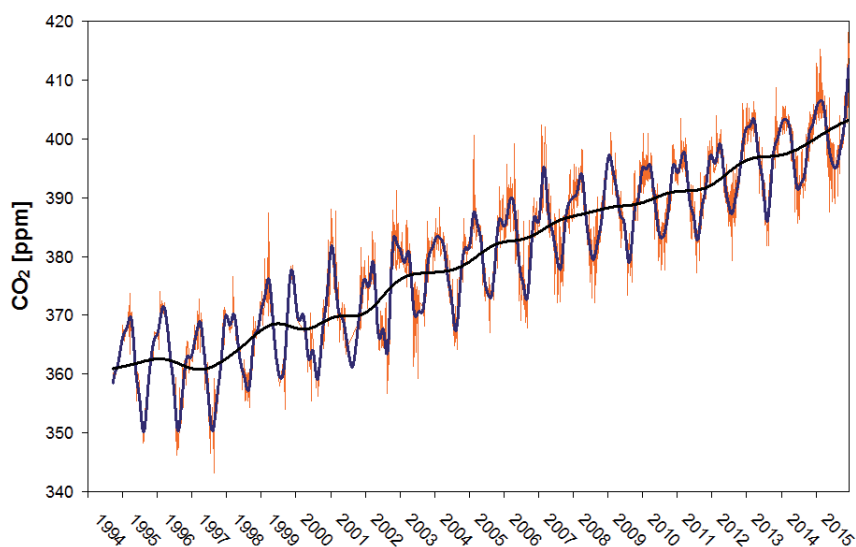


Figure 2. The record of CO<sub>2</sub> mixing ratios available for the Kasprowy Wierch station

Shown are daily means (in orange) calculated on the basis of raw measurement data, following application of an appropriate data-selection procedure. Daily means are smoothed using the CCGvu 4.40 routine (Thoning *et al.* 1989). The resulting curve is shown in dark blue. Also shown (in black) is the trend curve. See text for details.



The CO<sub>2</sub> trend curve for Kasprowy Wierch is compared in Figure 3 with those calculated for four other GHG monitoring stations located on the European continent: two stations representing regional marine background conditions (Mace Head, Ireland, 53°33' N, 9°80' E, 5 m a.s.l. and Terceira Island, Azores, Portugal, 38°77' N, 27°38' W, 19 m a.s.l.), and two continental stations (Hohenpeissenberg, Germany, 47°80' N, 11°02' E, 936 m a.s.l. and Pallas-Sammaltunturi, Finland, 67°97' N, 24°12' E, 560 m a.s.l.). The CO<sub>2</sub> trend curves for those stations were calculated using the same smoothing routine as in the case of Kasprowy Wierch (CCGvu 4.40 – Thoning *et al.* 1989), applied to the data retrieved from the NOAA ESRL Carbon Cycle Cooperative Global Air Sampling Network (<http://www.esrl.noaa.gov/gmd/dv/data/> – Dlugokencky *et al.* 2015). It is apparent from Figure 3 that mean rates of growth for the CO<sub>2</sub> mole fraction observed at five GHG monitoring stations in Europe are very similar (Kasprowy Wierch – 1.99 ppm year<sup>-1</sup>; Mace Head – 2.00 ppm year<sup>-1</sup>; Terceira Island – 1.97 ppm year<sup>-1</sup>; Hohenpeissenberg – 2.06 ppm year<sup>-1</sup>; Pallas-Sammaltunturi – 2.16 ppm year<sup>-1</sup>). The sustained difference of ca. 3 ppm between values noted at the marine background stations and at the Pallas-Sammaltunturi station may stem from the reduced role of the biospheric sink at high northern latitudes, as a factor controlling atmospheric mixing ratios of CO<sub>2</sub> in this region.

A distinct seasonal cycle is to be noted for the CO<sub>2</sub> mole fraction and the Kasprowy Wierch data (cf. Fig. 2), with higher values in winter and lower values in summer. This cycle is driven by seasonal photosynthetic activity of the biosphere. In the period in question, the peak-to-peak amplitude to the seasonal fluctuations of CO<sub>2</sub> mixing ratios measured at this site ranged between 12.8 ppm (2003) and 20.9 ppm (2001). The low

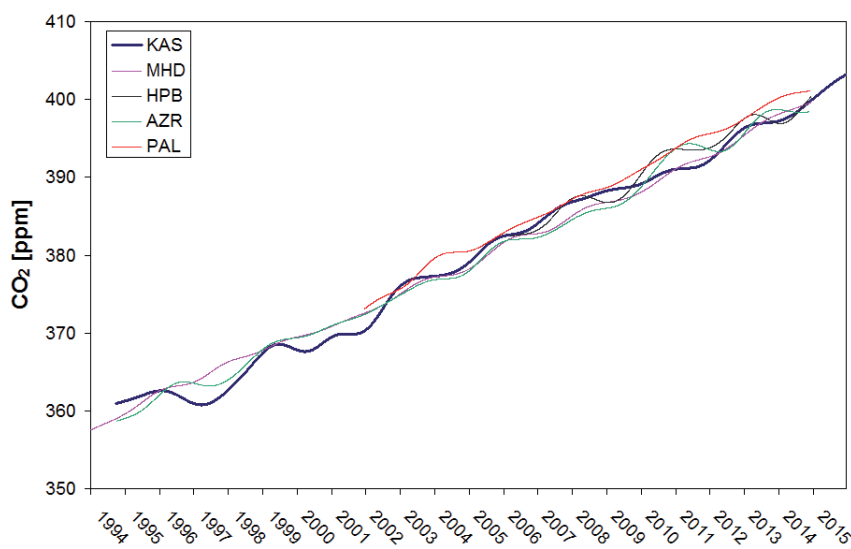


Figure 3. Comparison of CO<sub>2</sub> trend curves calculated for five European GHG monitoring stations  
KAS – Kasprowy Wierch, Poland; MHD – Mace Head, Ireland; HPB – Hohenpeissenberg, Germany; AZR – Terceira Island, Azores; PAL – Pallas-Sammaltunturi, Finland.



amplitude in 2003 can be attributed to a very hot summer in Europe that reduced photosynthetic activity in the biosphere regionally (Ciais *et al.* 2005).

Figure 4 compares mean seasonal cycles of atmospheric CO<sub>2</sub> mixing ratios measured at the five European GHG monitoring stations (Mace Head, Terceira Island, Hohenpeissenberg, Kasprowy Wierch and Pallas-Sammaltunturi). After the detrending procedure had been applied to daily means, monthly mean CO<sub>2</sub> mixing ratios were calculated for the period 2007–2014 for each station. As seen in Figure 4, there are distinct differences between the marine and continental stations, with respect to both the amplitude characterising the seasonal CO<sub>2</sub> cycle and the timing of maximum and minimum values for the CO<sub>2</sub> mixing ratio in the course of a year. Marine stations show a reduced peak-to-peak amplitude of the seasonal CO<sub>2</sub> cycle (Mace Head – 14.8 ppm; Terceira Island – 10.5 ppm) as compared with continental stations (Hohenpeissenberg – 22.7 ppm; Pallas-Sammaltunturi – 17.5 ppm). The amplitude of the CO<sub>2</sub> seasonal cycle at the Kasprowy Wierch station (14.3 ppm) is similar to that observed at Mace

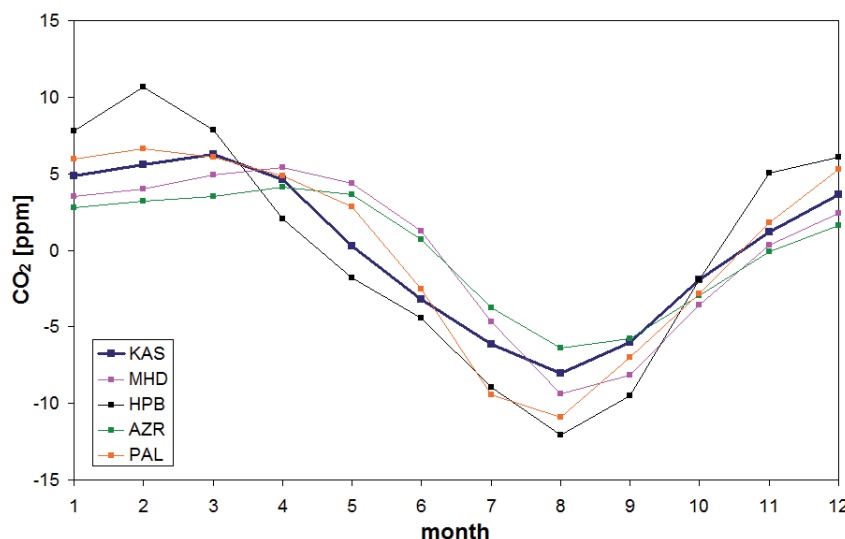


Figure 4. Mean seasonal CO<sub>2</sub> cycle at the five European GHG monitoring stations

KAS – Kasprowy Wierch, Poland; MHD – Mace Head, Ireland; HPB – Hohenpeissenberg, Germany; AZR – Terceira Island, Azores; PAL – Pallas-Sammaltunturi, Finland. Shown is the mean seasonal CO<sub>2</sub> cycle for the period 2007–2014 following removal of the trend. Typical uncertainties associated with the data points are in the range 0.1–0.6 ppm.

Head and Terceira Island. Reduced CO<sub>2</sub> amplitude at this site when compared to other continental stations is related to its high elevation. The seasonal maximum for the CO<sub>2</sub> mole fraction is recorded at marine stations in April, and is shifted towards the beginning of a year at continental sites, i.e. February at Hohenpeissenberg and Pallas-Sammaltunturi and March at Kasprowy Wierch. The minimum CO<sub>2</sub> mole fraction is recorded at all five stations during the month of August. These differences in the mean

seasonal CO<sub>2</sub> cycle between marine and continental stations stem from regional and local factors such as the varying role of anthropogenic emissions in terms of timing and intensity, and differences in the biospheric sink within the footprints of the discussed GHG monitoring sites.

## METHANE

Figure 5 shows the available record for atmospheric CH<sub>4</sub> mixing ratios measured at the Kasprowy Wierch station. Daily means for CH<sub>4</sub> mixing ratios are shown, as calculated following the application of a three-step data-selection procedure to raw measurement data. That procedure is aimed at selecting data representative of background conditions at this station (Nęcki *et al.* 2003). Also shown is the trend curve calculated on the basis of daily means using the CCGvu 4.40 smoothing routine (Thoning *et al.* 1989).

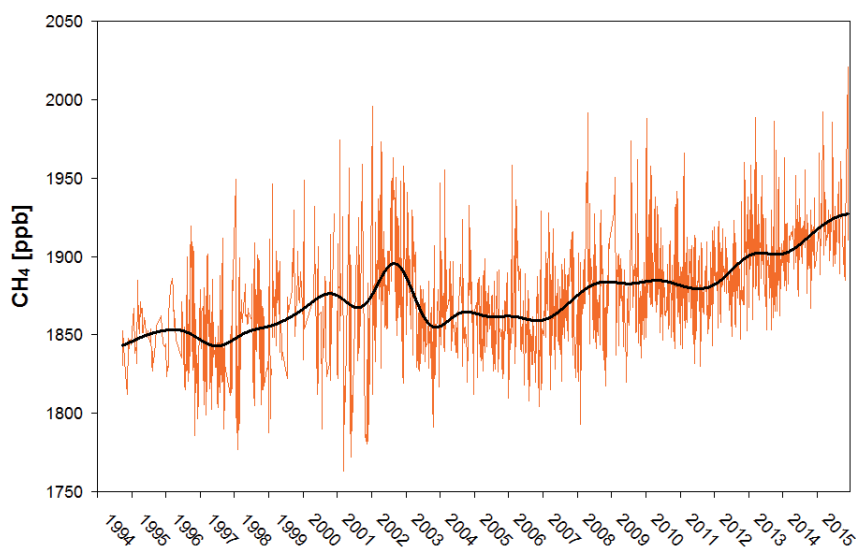


Figure 5. The record of CH<sub>4</sub> mixing ratios available for the Kasprowy Wierch station. Shown are daily means (in orange) calculated following the application to the raw measurement data of an appropriate data-selection procedure. The trend curve is also shown (in black). See text for details.

The mole fraction of atmospheric CH<sub>4</sub> measured at Kasprowy Wierch has increased from 1843 ppb in 1994 to 1927 ppb in 2015. The data for methane are also seen to differ from those on CO<sub>2</sub> in not manifesting a seasonal cycle. Furthermore, the long-term trend is generally more variable than in the case of CO<sub>2</sub>, with annual growth rates varying from  $-32.9$  ppb year<sup>-1</sup> in 2003 to  $+18.3$  ppb year<sup>-1</sup> in 2012.

Figure 6 summarizes the trend curves calculated for CH<sub>4</sub> mixing ratio records available for four European GHG monitoring stations (Mace Head, Terceira Island, Kasprowy Wierch and Pallas-Sammaltunturi). The trend curves for Mace Head, Terceira

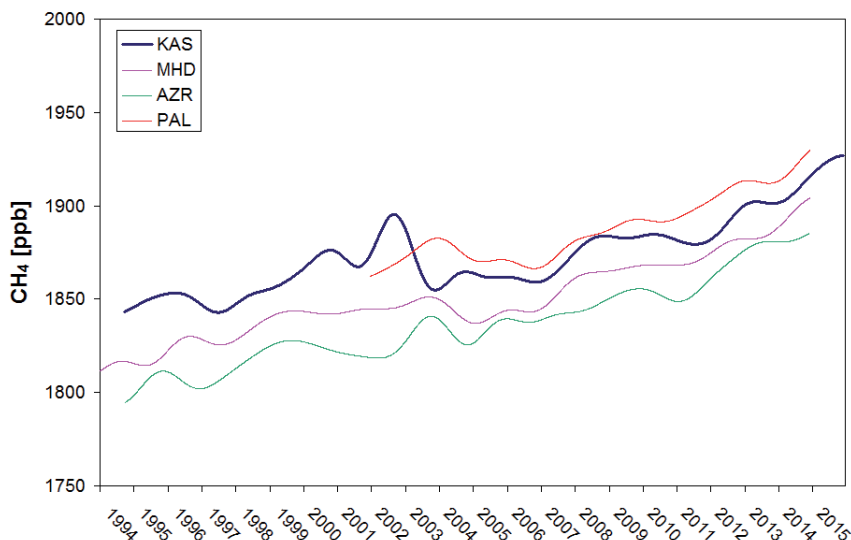


Figure 6. Comparison of  $\text{CH}_4$  trend curves calculated for the European GHG monitoring stations KAS – Kasprowy Wierch, Poland; MHD – Mace Head, Ireland; AZR – Terceira Island, Azores; PAL – Pallas-Sammaltunturi, Finland.

Island and Pallas-Sammaltunturi were calculated on the basis of data retrieved from the NOAA ESRL Carbon Cycle Cooperative Global Air Sampling Network (<http://www.esrl.noaa.gov/gmd/dv/data/> – Dlugokencky *et al.* 2015a). Following stagnation during the 2001–2007 period, the atmospheric mixing ratios for  $\text{CH}_4$  have begun to increase again in the recent years. This is a world-wide phenomenon, attributed to increased surface emissions of  $\text{CH}_4$ , mainly by wetlands in tropical South America and in boreal Eurasia (Bousquet *et al.* 2011). It is clear from Figure 6 that mole fractions of  $\text{CH}_4$  recorded at Kasprowy Wierch and Pallas-Sammaltunturi are shifted towards higher levels than is the case at the marine reference stations (Mace Head and Terceira Island). For Kasprowy Wierch, the departure has so far varied within the range 9.2 ppb in 2003 to 62.4 ppb in 2002. The higher mixing ratios for  $\text{CH}_4$  recorded at Kasprowy Wierch, as opposed to Mace Head, reflect continental emissions and a gradual loading with  $\text{CH}_4$  of air masses on their way from the Atlantic coast towards the centre of the European continent. The  $\text{CH}_4$  trend curve for the Pallas-Sammaltunturi station is shifted by ca. 15 ppb towards higher  $\text{CH}_4$  mixing ratios, as compared with the Kasprowy Wierch data. This offset is expected, and reflects the combined influence of: (i) high  $\text{CH}_4$  emissions originating from wetlands in high-latitude Eurasia, (ii) anthropogenic sources (mainly located in European parts of Russia), and (iii) reduced intensity of  $\text{CH}_4$  sinks in the polar atmosphere (Aalto *et al.* 2007). The origin of the anomalously high  $\text{CH}_4$  mole fractions recorded at Kasprowy Wierch in 2002 is unclear, and needs to be investigated further. Such a distinct maximum in

the  $\text{CH}_4$  mole fraction was not observed at this time at any other GHG monitoring station in Europe.

## NITROUS OXIDE

The  $\text{N}_2\text{O}$  record available to date for the Kasprowy Wierch station is as presented in Figure 7. Daily means for  $\text{N}_2\text{O}$  mixing ratios measured at this station, and the resulting  $\text{N}_2\text{O}$  trend curve, are compared in this figure with the trend curve for Mace Head, calculated on the basis of the data available for this station (<http://agage.eas.gatech.edu>, Prinn *et al.* 2000). As in the case of  $\text{CH}_4$ , continental emissions of  $\text{N}_2\text{O}$  result in an apparent departure of readings for Kasprowy Wierch from those characterising Mace Head, of the order of 1 ppb. The observed long-term growth rate is equal to  $0.83 \text{ ppb year}^{-1}$  and is similar to the globally averaged value of  $0.73 \text{ ppb year}^{-1}$  (IPCC 2013). The reason behind this growth is the imbalance in the global  $\text{N}_2\text{O}$  budget, caused mainly by enhanced fugitive emissions from internal metabolic processes of terrestrial and marine microorganisms (e.g. nitrifying and denitrifying bacteria). These emissions are directly related to the availability of reactive nitrogen compounds in a wide range of ecosystem types. This availability has increased drastically in the 20<sup>th</sup> century, following the industrialization of the Haber-Bosch process. As the rate of transport between the troposphere and the stratosphere (where  $\text{N}_2\text{O}$  is destroyed by photolysis) is too slow to respond to the rising levels of  $\text{N}_2\text{O}$ , a long-term increase in the concentration of this gas is to be observed.

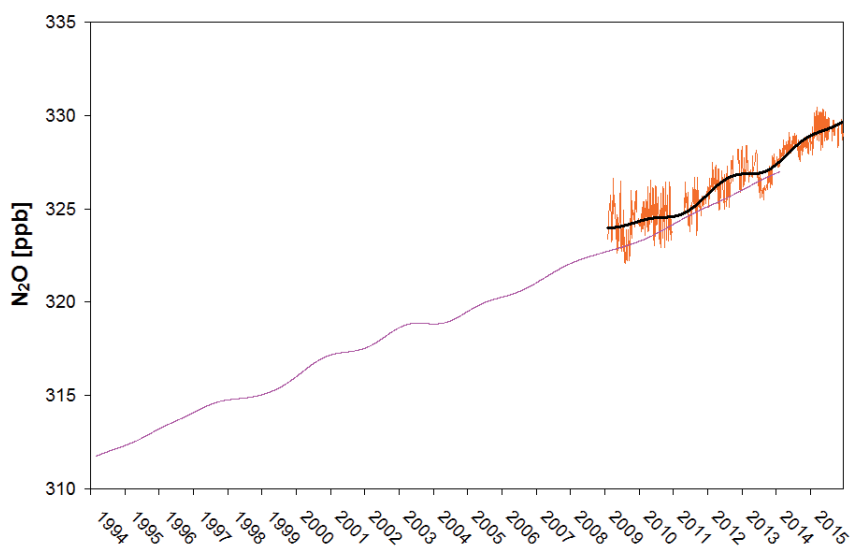


Figure 7. The record of  $\text{N}_2\text{O}$  mixing ratios available for the Kasprowy Wierch station. Shown are daily means (in orange) calculated following application to the raw measurement data of an appropriate data-selection procedure. Also shown are trend curves for Kasprowy Wierch (thick line in black) and the Mace Head station (thin line in magenta).

## GREENHOUSE GASES IN THE URBAN ATMOSPHERE

Urban areas are characterized by a high density of GHG sources. Local transport and heating systems release considerable amounts of  $\text{CO}_2$  arising from the burning of fossil fuels. Globally, the emissions of  $\text{CO}_2$  from fossil-fuel burning and cement production have increased by about 59%, from 22.4  $\text{PgCO}_2$  in 1990 to 35.9  $\text{PgCO}_2$  in 2014 (*Global Carbon Project* 2015). Urbanised regions are also major emitters of  $\text{CH}_4$ , which leaks from gas distribution networks and local landfills (Zimnoch *et al.* 2010). In urban areas located at mid and high latitudes, the intensity of GHG emissions can be modulated seasonally. The winter season is usually characterized by enhanced  $\text{CO}_2$  emissions due to fossil-fuel burning for heating purposes, while increased emissions of  $\text{CH}_4$  are expected from landfills and wetlands during the summer season.

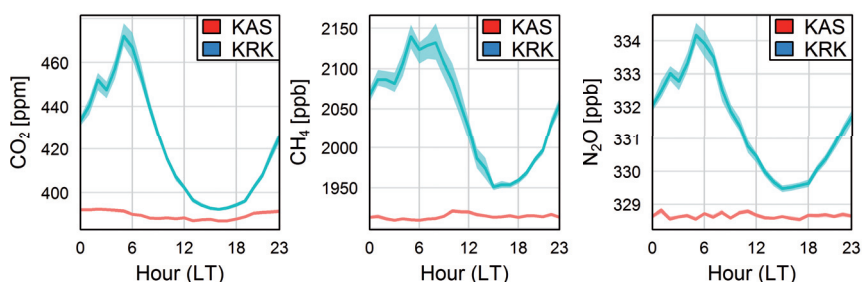


Figure 8. Mean diurnal cycle for the  $\text{CO}_2$ ,  $\text{CH}_4$  and  $\text{N}_2\text{O}$  mole fractions recorded at the Kasprowy Wierch (KAS) and Krakow (KRK) stations between July 10<sup>th</sup> and August 10<sup>th</sup> 2014

Thick lines represent mean values of hourly binned measurements. Shaded areas represent the  $1\sigma$  uncertainty range.

A high intensity of surface emissions of greenhouse gases in urban areas combines with distinct diurnal changes in the intensity of vertical mixing in the lower atmosphere, to produce the characteristic changes in GHG mixing ratios that are recorded in the near-ground urban atmosphere in the course of a day. High mole fractions of trace gases emitted from the surface are usually recorded during night hours, when a nocturnal inversion layer develops, while daily GHG minima are usually observed at midday and in the early afternoon hours, when vertical mixing of the lower atmosphere is at its maximum. An example of diurnal changes in  $\text{CO}_2$ ,  $\text{CH}_4$  and  $\text{N}_2\text{O}$  mixing ratios measured in Krakow and Kasprowy Wierch is shown in Figure 8. The diagram depicts mean diurnal variations in  $\text{CO}_2$ ,  $\text{CH}_4$  and  $\text{N}_2\text{O}$  mixing ratios in the Krakow atmosphere calculated for the one-month period between July 10<sup>th</sup> and August 10<sup>th</sup>, 2014. While distinct midday minima are observed for all three gases in Krakow,  $\text{CO}_2$ ,  $\text{CH}_4$  and  $\text{N}_2\text{O}$  values recorded at Kasprowy Wierch reveal broad maxima at this time. These are associated with diurnal changes in atmospheric circulation in the vicinity of the station (the mountain breeze). In the course of the day, air masses from the nearby town of

Zakopane that are loaded with greenhouse gases emitted from the surface (within the city and its surroundings) are lifted along the main valleys towards the mountain ridges, leading to the elevation of values for the mixing ratios that are recorded at the Kasprowy Wierch site (Nęcki *et al.* 2003, Gałkowski 2015).

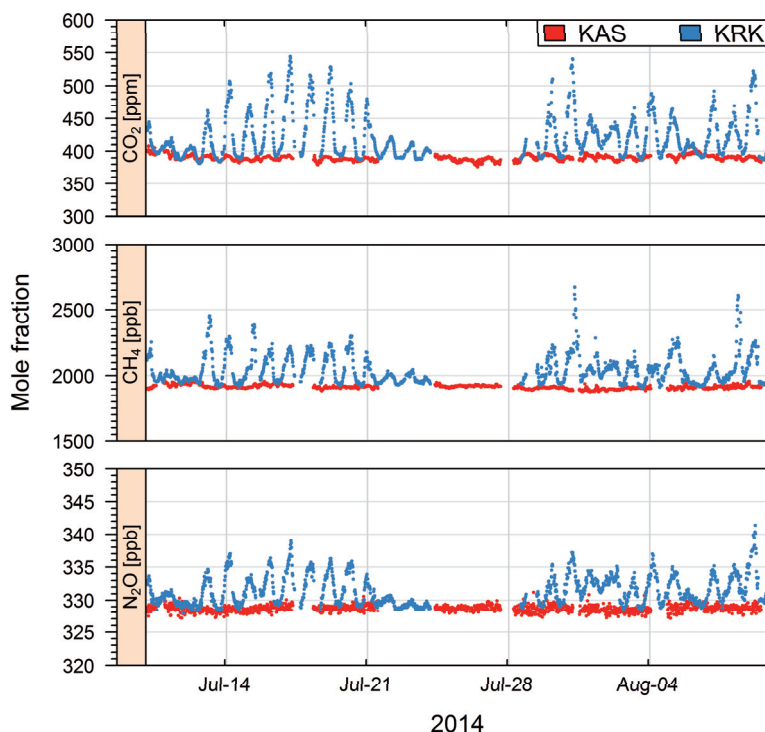


Figure 9. Daily variations of  $\text{CO}_2$ ,  $\text{CH}_4$  and  $\text{N}_2\text{O}$  mixing ratios recorded at the Krakow (blue) and Kasprowy Wierch (red) stations, between July 10<sup>th</sup> and August 10<sup>th</sup> 2014

Figure 9 shows the  $\text{CO}_2$ ,  $\text{CH}_4$  and  $\text{N}_2\text{O}$  mole fractions recorded at Krakow and Kasprowy Wierch in a single month. As Figure 9 makes clear, the local enhancements of  $\text{CO}_2$ ,  $\text{CH}_4$  and  $\text{N}_2\text{O}$  in the Krakow atmosphere during the night hours can be substantial. The presented record includes night-time mixing ratios exceeding the baseline level by up to 40% in the case of  $\text{CO}_2$  and  $\text{CH}_4$ , and ca. 3% for  $\text{N}_2\text{O}$ .

## CONCLUSIONS

Long-term, systematic observations of atmospheric levels of the major greenhouse gases allow for quantification of their temporal evolution under growing anthropogenic stress. They also allow for a deeper insight into the processes controlling the levels of these gases in the continental atmosphere over different time scales. In fact, several

important characteristics are revealed from the presentation here of the way the atmospheric mixing ratios for  $\text{CO}_2$ ,  $\text{CH}_4$  and  $\text{N}_2\text{O}$  over Europe and the adjacent portions of the Atlantic Ocean have evolved.

First, the growth rates for the  $\text{CO}_2$  mole fraction recorded at stations both marine (Mace Head, Ireland; Terceira Island, Azores) and continental (Hohenpeissenberg, Germany; Kasprowy Wierch, Poland; Pallas-Sammaltunturi, Finland) reveal only small temporal changes and almost coincide, leading to a quasi-linear increase in the  $\text{CO}_2$  mole fraction over the European continent as a whole. While values for the  $\text{N}_2\text{O}$  mole fraction also display steady growth over this time period, the mole fractions characterising  $\text{CH}_4$ , has been increasing again over the past several years, following a 2001–2007 stagnation period.

Second, the mean seasonal  $\text{CO}_2$  cycle reveals distinct differences among the monitoring sites considered, depending on the location of the given station, and as a reflection of differences in seasonal biospheric impact and the extent of surface anthropogenic emissions of this gas. The weak seasonality characterising the  $\text{CH}_4$  and  $\text{N}_2\text{O}$  records for Mace Head is hardly noted in the centre of the continent. It is also possible to note a distinct offset between the trend curve for  $\text{CH}_4$  mixing ratios measured at Kasprowy Wierch, and those representing the marine (Mace Head and Terceira Island) reference stations. The mean size of the departure involved in the case of  $\text{CH}_4$  is 27.3 ppb over the 1995–2014 period, and is a reflection of continental emissions of  $\text{CH}_4$  linked mainly to anthropogenic activities (leaks from natural-gas distribution networks, landfills and livestock). For  $\text{N}_2\text{O}$ , a similar if far smaller departure, of the order of 1 ppb, is to be observed for the 2009–2014 period.

Comparison of quasi-continuous measurements of  $\text{CO}_2$ ,  $\text{CH}_4$  and  $\text{N}_2\text{O}$  mixing ratios made in the urban atmosphere of Krakow and at the regional reference site of Kasprowy Wierch, i.e. locations approximately 100 km apart, allows for a deeper insight into the mechanisms controlling daily variations in the atmospheric mixing ratios of these gases at the two sites. Development of a nocturnal inversion layer in the atmosphere above the city leads to local enhancements of  $\text{CO}_2$ ,  $\text{CH}_4$  and  $\text{N}_2\text{O}$  mole fractions in the Krakow atmosphere during night hours, significantly exceeding the baseline level. Daily fluctuations of  $\text{CO}_2$  and  $\text{CH}_4$  mixing ratios recorded at Kasprowy Wierch are shifted in phase (daily maxima and nocturnal minima), and are much weaker than those observed in Krakow. They are related to local circulation of the atmosphere, bringing air with higher mixing ratios of  $\text{CO}_2$  and  $\text{CH}_4$  from the surrounding valleys up to the station during daytime. During the night, the station is often situated above the nocturnal inversion layer.

## ACKNOWLEDGMENTS

The authors wish to thank the numerous individuals and institutions which have supported the measurement of the trace-gas composition of the atmosphere over southern Poland in the past twenty years. The ongoing monitoring activities are supported by the



EU FP7 InGOS project, as well as Poland's Ministry of Science and Higher Education (statutory funds, project no. 11.11.220.01).

## REFERENCES

- Aalto T., Hatakka J., Lallo M., 2007, *Tropospheric methane in northern Finland: seasonal variations, transport patterns and correlations with other trace gases*, Tellus, 59B, 251–259.
- Bousquet P., Ringeval B., Pison I., Dlugokencky E.J., Brunke E.-G., Carouge C., Chevalier F., Fortems-Cheiney A., Frankenberg C., Hauglustaine, D.A., Krummel P.B., Langenfelds R.L., Ramonet M., Schmidt M., Steele L.P., Szopa S., Yver C., Viovy N., Ciais P., 2011, *Source attribution of the changes in atmospheric methane for 2006–2008*, Atmos. Chem. Phys., 11, 3689–3700.
- Chmura Ł., Róžański K., Nęcki J.M., Zimnoch M., Korus A., Pycia M., 2008, *Atmospheric concentration of carbon dioxide in southern Poland: comparison of mountain and urban environments*, Pol. J. Environ. Stud., 17, 859–867.
- Chmura Ł., 2009, *Greenhouse gases in the atmosphere over southern Poland; temporal and spatial variability during the period 1994–2007*, PhD Thesis, AGH University of Science and Technology, Kraków (in Polish).
- Ciais P., Reichstein M., Viovy N., Granier A., Ogée J., Allard V., Aubinet M., Buchmann N., Bernhofer Chr., Carrara A., Chevalier F., De Noblet N., Friend A.D., Friedlingstein P., Grünwald T., Heinesch B., Keronen P., Knohl A., Krinner G., Loustau D., Manca G., Matteucci G., Miglietta F., Ourcival J.M., Papale D., Pilegaard K., Rambal S., Seufert G., Soussana J.F., Sanz M.J., Schulze E.D., Vesala T., Valentini R., 2005, *Europe-wide reduction in primary productivity caused by the heat and drought in 2003*, Nature, 437, 529–533.
- CUCUMBER 2016, Website of the CUCUMBER intercomparison programme, <http://cucumbers.uea.ac.uk/>, accessed on 18.03.2016
- Dlugokencky E.J., Lang P.M., Masarie K.A., Crotwell A.M., Crotwell M.J., 2015, *Atmospheric carbon dioxide dry air mole fractions from the NOAA ESRL Carbon Cycle Cooperative Global Air Sampling Network, 1968–2014*, Version: 2015-08-03, [ftp://aftp.cmdl.noaa.gov/data/trace\\_gases/co2/flask/surface/](ftp://aftp.cmdl.noaa.gov/data/trace_gases/co2/flask/surface/)
- Dlugokencky E.J., Lang P.M., Crotwell A.M., Masarie K.A., Crotwell M.J., 2015a, *Atmospheric methane dry air mole fractions from the NOAA ESRL Carbon Cycle Cooperative Global Air Sampling Network, 1983–2014*, Version: 2015-08-03, [ftp://aftp.cmdl.noaa.gov/data/trace\\_gases/ch4/flask/surface/](ftp://aftp.cmdl.noaa.gov/data/trace_gases/ch4/flask/surface/)
- Galkowski M., 2015, *Temporal and spatial variability of nitrous oxide in the atmosphere over Malopolska region: determination of loads and emissions*, PhD Thesis, AGH University of Science and Technology, Kraków.
- Global Carbon Project, 2015, Carbon budget and trends 2015, <http://www.globalcarbonproject.org/carbonbudget>, accessed on 18.03.2016.
- IPCC, 2013, *Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change*, Cambridge, United Kingdom and New York, NY, USA, Cambridge University Press.

- Keeling Ch.D., 1960, *The concentration and isotopic abundances of carbon dioxide in the atmosphere*, Tellus, 12, 200–203.
- Nassar R., Sioris C.E., Jones D.B.A., McConnell J.C., 2014, *Satellite observations of CO<sub>2</sub> from a highly elliptical orbit for studies of the Arctic and boreal carbon cycle*, J. Geophys. Res. Atmos., 119, 2654–2673.
- Nęcki J.M., Schmidt M., Róžański K., Zimnoch M., Korus A., Lasa J., Graul R., Levin I., 2003, *Six-year record of atmospheric carbon dioxide and methane at a high-altitude mountain site in Poland*, Tellus, 55B, 94–104.
- Prinn R.G., Weiss R.F., Fraser P.J., Simmonds P.G., Cunnold D.M., Alyea F.N., O'Doherty S., Salameh P., Miller B.R., Huang J., Wang R.H.J., Hartley D.E., Harth C., Steele L.P., Sturrock G., Midgley P.M., McCulloch A., 2000, *A history of chemically and radiatively important gases in air deduced from ALE/GAGE/AGAGE*, J. Geophys. Res., 105(D14), 17751–17792.
- Takagi H., Saeki T., Oda T., Saito M., Valsala V., Belikov D., Saito R., Yoshida Y., Morino I., Uchino O., Andres R.J., Yokota T., Maksyutov S., 2011, *On the benefit of GOSAT observations to the estimation of regional CO<sub>2</sub> fluxes*, SOLA, 7, 161–164.
- Thoning K.W., Tans P.P., Komhyr W.D., 1989, *Atmospheric carbon dioxide at Mauna Loa Observatory 2. Analysis of the NOAA GMCC data, 1974–1985*, J. Geophys. Res., 94, 8549–8565.
- WMO 2013. GAW Report No. 213, *17th WMO/IAEA Meeting on Carbon Dioxide, Other Greenhouse Gases and Related Tracers Measurement Techniques (GGMT-2013)*, Beijing, China, 10–13 June 2013, World Meteorological Organization, Geneva, Global Atmosphere Watch.
- Zimnoch M., Godłowska J., Nęcki J.N., Róžański K., 2010, *Assessing surface fluxes of CO<sub>2</sub> and CH<sub>4</sub> in urban environment: a reconnaissance study in Krakow, Southern Poland*, Tellus 62B, 573–580.
- ([www.esrl.noaa.gov/gmd/obop/mlo/](http://www.esrl.noaa.gov/gmd/obop/mlo/))
- ([www.wmo.int/pages/prog/gaw](http://www.wmo.int/pages/prog/gaw))
- ([www.esrl.noaa.gov/gmd/](http://www.esrl.noaa.gov/gmd/))
- ([www.agage.eas.gatech.edu](http://www.agage.eas.gatech.edu/))
- ([www.icos-infrastructure.eu](http://www.icos-infrastructure.eu))
- ([www.neonscience.org](http://www.neonscience.org))
- (<http://www.esrl.noaa.gov/gmd/dv/data/>)